

Analysis of the Spatial Variation of Crosslink Density in Superabsorbent Polymers

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INTRODUCTION

Superabsorbent polymers are often designed with increased density of crosslinking in the outer layer of the particles in order to improve liquid retention under load. For efficient product design, it is desirable to directly measure the spatial variation in crosslink density. Typically employed techniques (solvent uptake or measuring the changes in various mechanical properties such as the modulus) do not normally provide spatially resolved crosslink density information. We have applied Scanning Transmission X-ray Microscopy (STXM) to examine the swelling of inhomogenously crosslinked superabsorbent polymers in deionized water and salt water solution.

STXM is an effective way to study the chemical and morphological character of polymers on a sub micron spatial scale.¹ STXM image contrast is based on core electron excitation by x-ray absorption; an interaction that has remarkable chemical sensitivity.^{1,2} Beam damage is less than in TEM microscopes² and samples can be examined in wet and in ambient conditions.

EXPERIMENTAL

The XM-1 conventional (BL 6.1) as well as the scanning transmission x-ray microscopes (STXM) at the Advanced Light Source (BL 7.0)³ and the National Synchrotron Light Source (X1A) were used in this study.

The super absorbent polymer samples were approximately 0.3 mm diameter spherical beads of polyacrylic acid lightly crosslinked throughout. Samples A and B were 80% neutralized with NaOH. All three samples were more heavily crosslinked in the outer shell by reaction of the spheres with ethylene glycol diglycidyl ether (EGDE). Sample A was reacted with half as much crosslinking agent (EGDE) as the other samples.

RESULTS

Figure 1 presents a simplified schematic of the wet cell used for this work. Similar wet cells have been used in X-ray microscopes for examining biological materials, clay particles and manganese nodules in wet environments.⁵ The hydrated sample is sandwiched between two ~ 100 nm thick Si_3N_4 windows, and the water thickness is controlled by compression of the front and back cell halves.

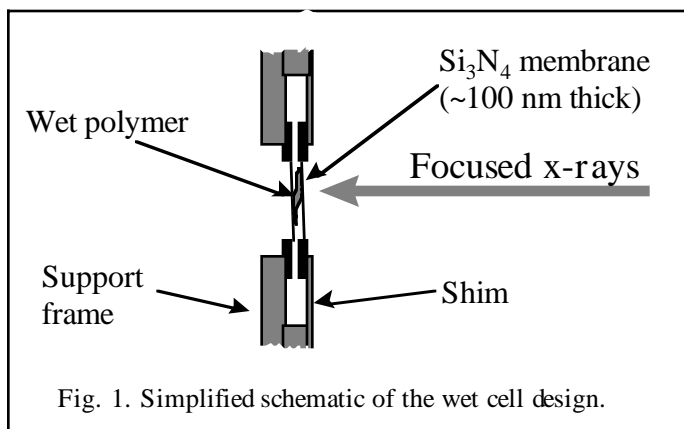


Fig. 1. Simplified schematic of the wet cell design.

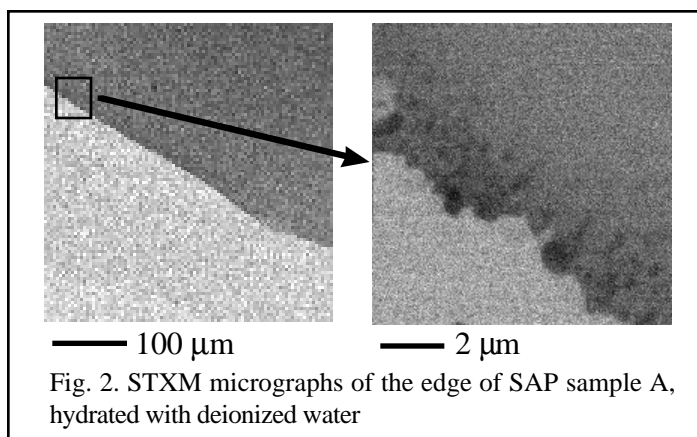


Fig. 2. STXM micrographs of the edge of SAP sample A, hydrated with deionized water

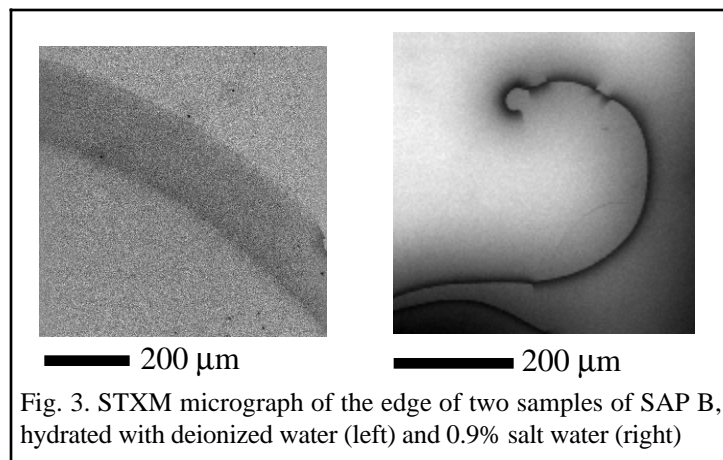


Fig. 3. STXM micrograph of the edge of two samples of SAP B, hydrated with deionized water (left) and 0.9% salt water (right)

The results for two different SAP polymers are presented in Figures 2 and 3. In both polymers, the surface region of the SAP sections were crosslinked, but twice as much crosslinker was used for sample B than for sample A. Figure 2 presents a STXM image of the edge of SAP section A, hydrated with deionized water. In the higher resolution image, small dark features are observed near the edge of the section. In this instance, the decreased x-ray transmission corresponds to an increased polymer density, which is a consequence of a higher crosslink density. Figure 3 (left-hand image) presents the edge of water-hydrated SAP section B, which has twice the crosslinker as section A. In this image, a ~ 150 μm wide band of higher density polymer is observed at the section edge. The image on the right-hand side of Figure 3 is of the edge of a sample of SAP B hydrated with 0.9% salt-water solution. A narrower band of higher density is

observed at the edge of this polymer and has broken loose from the core polymer. Both the center and the more crosslinked edge of this polymer do not expand as much in salt solution as in deionized water solution.

We have also had success in analyzing core / shell structured SAP material which has been wetted and dried onto an Si_3N_4 window using the XM-1 microscope at the ALS. The advantages in using XM-1 include the facile sample mounting and ease and speed in obtaining images. Since one is

constrained to relatively large magnifications on this microscope compared to STXM, several images in a line across the edge of the sample were obtained and pasted together in a montage to cover the interesting area of the sample.

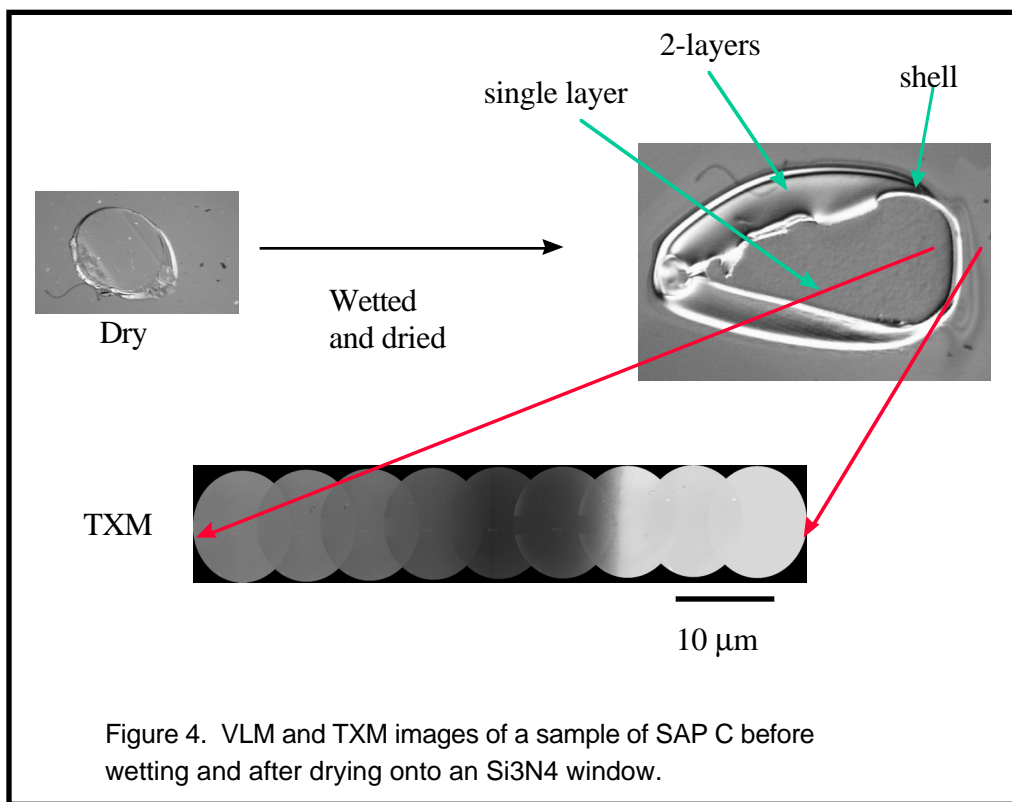


Figure 4 presents the VLM and the TXM results for a thin section of an acid form core/shell bead which was wetted with de-ionized water and dried on a Si₃N₄ window. At top left is a VLM image of the section prior to wetting it. The section is oblong in shape because of a small amount of compression which occurred in the direction of cutting during microtoming. There was some debris on the window before the section was added and which we were not able to remove. A montage of TXM images obtained from this sample is shown at the bottom. The VLM image collected before the TXM imaging is presented in the upper right.

The wetted and dried section in Figure 4 had an interesting shape. Because the outer shell of the sample was crosslinked, it did not swell as much as the central part of the section. When the inner part of the sample disk swelled, it apparently expanded past the shell. The shell can be seen as the band closest to the middle of the sample. The sample is shaped something like a bedroom slipper with polymer folded over and therefore forming two layers (one atop the other) on each side at the toe end. Although there was a good deal of variation in shape from one sample to another after sections were wetted and dried, shapes similar to this with the shell remaining much less expanded than the core polymer were seen fairly often.

From the VLM images in Figure 4 one can see that the polymer section remains at least partly expanded (radially) after wetting and drying. It is difficult to determine by VLM the size of the wet polymer after swelling because of the refraction effects of the water. If the polymer does not shrink laterally during dehydration, then the thickness of the polymer after being wetted and dried

is also a useful measure of the polymer density in the swollen polymer gel. In the TXM montage in Figure 4 there is a band about 16 μm wide of material which is more x-ray absorbing, near the center of the image and at the edge of the sample which we identify as the shell.

CONCLUSIONS

We have shown that STXM can be used to visualize the core / shell structure of hydrated SAP prepared by chemically crosslinking the surface of SAP beads. Conventional and scanning TXM can provide information on the internal structure (or strength) of thin sections of SAP materials which have been wetted in DI water, as well as those wetted and allowed to dry.

ACKNOWLEDGMENTS

The x-ray microscope XM-1 at the Advanced Light Source is supported by the United States Department of Energy, Office of Basic Energy Sciences under contract DE-AC 03-76SF00098. The ALS STXM and the Advanced Light Source are supported by the United States Department of Energy, Office of Basic Energy Sciences under contract DE-AC 03-76SF00098. The X-1A STXM was developed by the group of Janos Kirz and Chris Jacobsen at SUNY Stony Brook with support from the Office of Biological and Environmental Research, U.S. DoE under contract DE-FG02-89ER60858, and the NSF under grant DBI-9605045. U. Neuhaeusler would like to thank the German Academic Exchange Service for financial support.

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